**List of changes in the revised manuscript and detailed** **responses on the editorial comments**

**Editorial comments:**  
  
1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

**Thank You for this comment. The text of manuscript was checked and improved.**

2. Please revise lines 501-510, 517-518, 529-531, 533-536, 538-539, 540-541, 575-579 to avoid previously published text.

**We agree with this remark. The lines were corrected following:**

**501-510 (now: 654-663):** Two of an applied substrates are smooth and planar: silica and carbon surfaces, while the others have roughness and mesopores. The measured contact angles are discussed in relations to the microscopic wetting parameter, αw. This parameter emerges from a corresponding states rule of the partition function for this system, and is a measure of the ratio between the liquid–pore walls intermolecular interactions to the interactions of two liquid molecules22-24. Therefore, this parameter is a well-defined measure of wettability at the nano- and macro-scales. The αw parameter is shown to be a monotonic function of the contact angle. The results of measurements have found that contact angles for the rough surfaces were larger than those for the smooth planar surfaces for all studied liquids, including non-wetting and well-wetting liquids. These results suggest the Cassie-Baxter mechanism of wettability on nano-

**517-518 (now: 686-687):** f increases monotonically with an increase of αw parameter, what confirms a Cassie–Baxter model of wetting on rough substrates.

**529-531 (now: 698-700):** temperature dependence of capacitance C shows a sharp increase at T=260 K, corresponding to the melting of adsorbed D2O inside the pores of SBA-15 and at T=246.1 K, which refers to the melting of adsorbed water inside the pores of OMC. For both systems we observe the second

**533-536 (now: 702-705):** deuterated water. The observed signals come from both the bulk and the confined liquid, because the samples studied here are a suspension of filled porous matrices in the pure liquid. We can observe that the melting temperature of D2O in SBA-15 pores is depressed relative to the temperature of the bulk by ΔT=Tm,pore − Tm,bulk =- 16.5 K, while for OMC ΔT=- 30.4 K.

**538-539 (now: 707-708):** literature the melting temperature in the pores Tm,pore can be considered in terms of two variables: pore size H and wettability parameter αw. For smaller αw values (αw << 1) the

**540-541 (now: 708-710):** For smaller αw values (αw << 1) the depression of Tm,pore is expected. If the pore width H is the same, then the change in the αw value of the system affects on the change of the Tm,pore.

**575-579**: Revised and moved from the Conclusion section partially to Results and Discussion section.

3. Please remove the embedded figure(s) from the manuscript.

**The embedded figures were removed from the manuscript.**

4. Figures: Please line up the panels better. Some panels are off-set in Figure. Please ensure that the panels are of the same dimensions if possible. Please use consistent font size among panels in the same figure, if possible.

**Thank You for this remark. The changes were implemented.**

5. Please shorten the title if possible.

**The title was shorten. Now the manuscript is titled: Surface properties of synthesized nanoporous carbon and silica matrices; the melting of D2O confined inside these pores.**

6. Please add a Long Abstract (150-300 word) before Introduction section. It should include a statement about the purpose of the method. A more detailed overview of the method and a summary of its advantages, limitations, and applications is appropriate. Please focus on the general types of results acquired.

**The Long Abstract was added (lines: 34-54) (293 words).**

7. Please rephrase the Introduction to include a clear statement of the overall goal of this method.

**Thank You for the comment. The introduction was changed in following way:**

Gas adsorption is one of major importance for the characterization of a wide range of porous materials. Of all the many gases and vapours, which are available and may be used as adsorptives, nitrogen has remained universally properties. With the aid of user-friendly commercial equipment and data processing, it is now possible to use nitrogen adsorption at 77 K to determine nitrogen adsorption–desorption isotherms at 77 K in a wide range of p/p0. All the computational procedures for pore size analysis have limitations. The various assumptions include an ideal pore shape, rigidity of the structure and typical model (capillary condensation or micropore filling). The derived pore widths and pore volumes should be regarded as effective values with respect to the adsorption of nitrogen at 77 K. The surface characteristics related with surface chemistry of the materials depend on surface charge related with the heteroatoms or functional groups present on the surface. Measurements of the dielectric constant allow on the investigation of melting phenomena, as the polarizability of the liquid and solid phases are different from each other. A change in the slope of the temperature dependence of the capacitance shows that melting occurs in the system.

8. Please use SI abbreviations for all units: L, mL, µL, h, min, s, etc.

**The SI abbreviations were used in the manuscript.**

9. Please include a space between all numbers and their corresponding units: 15 mL, 37 °C, 60 s; etc.

**We improved it, including the spaces.**

10. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents. For example: Micromeritics Corp. Norcross, JEOL JEM-1400, JEOL JSM-7001F, KSV701, Solartron 1260, etc.

**All commercial language were removed and putted in the Table of Materials and Reagents.**

11. 3.1.1, 3.2.1, 3.3.1, 3.5.7, lines 295-297: Please write the text in the imperative tense as if telling someone how to do the technique (e.g., “Do this,” “Ensure that,” etc.).

**We used the imperative tenses in given places.**

12. 3.1.2: Please specify the mass of sample added.

**The mass was specified in line 243:**

* + 1. Fill the tube with the sample, weighing the mass of the sample c.a. 0.20 g.

13. 3.1.4: What does it mean by weighing the mass of the sample from 0.15 g to 0.20 g? Please clarify.

**The mass was specified in line 243:**

* + 1. Fill the tube with the sample, weighing the mass of the sample c.a. 0.20 g.

14. 3.1.5: Please describe how to degas the adsorbents.

**The additional explanation was added:**

**Lines 245-248**: Prior to the measurements, degas the adsorbents at 150 °C K for at least 24 hours. Glass tube with the sample place in degas port of ASAP analyzer. In the degassing port, the sample is connected to the vacuum (5µm Hg) and heated to the set temperature. After degassing, fill the sample with nitrogen and transfer to the analysis port.

15. 3.2.2: Please specify the sample mass and volume of ethanol added.

**The lines 255-256 were changed:**

3.2.2: In order to obtain a monodisperse film of the specimen, suspend 2-3 little grains of the sample in the 2 mL of ethanol and place in an ultrasonic bath for 3 h.

16. 3.3: Please change Elemental Analysis to Energy Dispersive X-Ray Spectroscopy.

**Thank You for this remark. The title was changed (line 261).**

17. 3.4.1: Please revise this sentence to be clear.

**The additional explanation was added:**

**Lines 272-275:** Potentiometric titration experiment perform by using an automatic burette, which allows to the adding of titrant by small and controlled portions (according to the titration software and procedure). An automatic Dosimat should provide the smallest increment at least 1 µL.

18. Please revise to explain the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc.

**The Representative Results were revised. The following explanations were added:**

**Lines 363-367**: From the position of an inflection point on sorption isotherms (Fig. 1 (A), (C)), we receive an information about the pressure at which the process of mesopores filling starts; the knowledge of the value of pressure is needed for calculation of mean pore size and pores size distribution (PSD) (Fig. 1 (B), (D)), applying for this the Kelvin equation.

**Lines 372-374**: An interpretation of TEM images allows to an estimation of pore sizes and to comparison the values with the data obtained from sorption measurements (Fig. 1).

**Lines 386-387**: An analysis of position of zero charge point on pH scale provides an information about an acidity in the system. As the value of the pH pzc is lower, the sample is more acidic.

**Lines 393-395**: The value of energy of characteristic radiation coming from the sample allows to an identification of elements including in the studied sample, while the intensity (the height of the peaks in the spectrum) enables to an quantified analysis (Fig. 4 (C)).

**Lines 412-416**: The wettability determines the surface acidity; this method with the potentiometric titration and an EDX analysis constitutes the full description of the surface properties of the sample. As the value of contact angle is lower, then the wettability is better, what means that an interaction of penetrating liquid molecule is more pronounced with the studied surface (Fig. 5 (A) – (B)).

**Lines 435-439**: The dielectric results show the temperature dependences of electric capacity for both samples (Fig. 7 (A) – (B)). The anomalies visible in the C(T) curves evidence about phase transitions occurring in the system. The localization of the anomaly position allows to determine the melting point both: of the bulk liquid as well as the melting point in the pores of studied sample.

19. As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:  
a) Critical steps within the protocol  
b) Any modifications and troubleshooting of the technique  
c) Any limitations of the technique  
d) The significance with respect to existing methods  
e) Any future applications of the technique

**The Discussion was revised. The following explanations were added:**

**Lines 511-529**: The critical steps during preparation the ordered mesoporous carbon material include: preparation the ordered mesoporous silica materials as the template with well-defined structural properties that affect the property of the final materials and tempering/carbonization step under nitrogen atmosphere. The modification of the typical method of preparation the mesoporous ordered silicates with cylindrical pores28 concerned the application the not typical structure directing agent Pluronic PE10500 polymer for improving the structural properties of material. The 3D interconnected and stable porous structure of the template is necessary for preparation the mesoporous carbon materials. Moreover, a key disadvantage is the essential requirement of the sample treatment for the template removal. The properties of chemicals used in this step can affect the carbon surface and its functionality. The presented strategy propose the preparation the negative replication of OMCs based on ordered mesoporous solid template. The pore size control and symmetric ordering are simply determined using the silica template and is not associated with interaction between the carbon precursor and the template. The literature show the potential of OMC for various electrochemical systems29-30. The impregnation mechanism presented in this work, is responsible for facile process to precisely replicate the negative structure of the silica template. The nature of the hard template procedure ensures the pyrolysis phenomena causing less damage to the regular and ordered structure. Moreover, this method allows the easier graphitization of the OMC materials formed within the solid template.

**Lines 543-554**: The critical steps during nitrogen adsorption/desorption measurement include the very precise mass sample definition and sufficient degas step. The measurement procedure was performed according appropriate guidelines of this procedure. Despite the fact that physisorption measurements are widely used for the determination of surface area and pore size distribution, the interpretation of the experimental isotherms is not always straightforward. During the computation of the mesopore size distribution, by application the modified Kelvin equation (which is base of the theory) it is necessarily to accept the assumption of the rigid and of well-defined shape of pores. Moreover, the range of validity of the Kelvin equation and the interpretation of hysteresis loops on the isotherms remain still unresolved problems. The possibility of facilitation are related to the application of empirical methods of isotherm analysis (e.g. the αs-method29-34). However, this manner require to utilize adsorption data obtained with non-porous reference materials.

**Lines 564-577:** The properties of the pore-network structure based on physical adsorption/desorption analyses is fundamental to thecharacterization of nanopowders and nanomaterials. Nitrogen adsorption/desorption methods can be regarded as the first stage in the characterization of microporous and mesoporous solids. The method is in general applicable to samples of all classes of porous bodies or materials. This method allows to estimate the porous structures based on the shapes of isotherms and hysteresis loops directly from experimental measurement. The nitrogen adsorption/desorption next to the other methods of porous structure determination (liquid intrusion35, Light, X-ray, and Neutron Scattering36-37 and microscopy32) is the most important and useful technique due to the wide applicability and mutual comparability of results. Nitrogen is typical considered a standard adsorptive molecule for pore characterization by gas adsorption method. It is possible to use other types of molecules (carbon dioxide, krypton, argon) could be applied for obtaining new information about the sample and the characterization of microporous materials.

**Lines 588-598**: Transmission electron microscopy is a significant analytical technique in the physical, chemical and biological sciences; TEM finds application in [cancer research](https://en.wikipedia.org/wiki/Cancer_research), [virology](https://en.wikipedia.org/wiki/Virology) and [materials science](https://en.wikipedia.org/wiki/Materials_science) as well as in [nanotechnology](https://en.wikipedia.org/wiki/Nanotechnology) and [semiconductor](https://en.wikipedia.org/wiki/Semiconductor) research. Transmission electron microscopy is capable of imaging at higher [resolution](https://en.wikipedia.org/wiki/Optical_resolution) than [light microscopes](https://en.wikipedia.org/wiki/Optical_microscope), owing to the smaller [de Broglie wavelength](https://en.wikipedia.org/wiki/De_Broglie_wavelength) of electrons. This enables to capture the details thousands of times smaller than a resolvable object seen in a light microscope. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. Therefore, one of the limitations of the method is that the specimen should be an ultrathin section less than 100 nm thick or a suspension on a grid. TEM can be modified into a [scanning transmission electron microscope](https://en.wikipedia.org/wiki/Scanning_transmission_electron_microscope) (STEM) by the addition of a system that rasters the beam across the sample to form the image, combined with suitable detectors.

**Lines 604-621**: The negatively charged sites increase the van der Waals interactions between the guest and host molecules on the SBA-15 surface improving the adsorption of the silica matrix. The critical steps during potentiometric titration measurement include the very precise addition the titrant to the suspension and ensuring their continuity of mixing. The potentiometric titration procedure was performed fully automatic for ensuring the most appropriate results. The important and unique step was also application of special software for controlling and calculations. The limitation of this method is the calibration step of the pH electrode and ensuring the stable atmosphere (for example nitrogen) and temperature. Potentiometric titration can be categorized as acid/base titration procedure. This technique requires measuring the voltage change during titrant addition steps. It provides an adaptable, affordable and highly accurate technique to achieve high purity which is essential to many fields, particularly pharmaceuticals and functional materials. Actual, exist a number of kinds of potentiometric titrations providing possibilities depending on the need for determining samples. Some of them include acid-base, redox, precipitation and complexometric techniques. Potentiometric titrations as automated systems ensure greater capacity for sample characterization. These features ensure the continued usefulness of potentiometric titrations methods in material chemistry.

**Lines 645-650**: EDX is one of the techniques, which determines the atomic composition of the specimen. It does not give chemical information (e.g. oxidation state, chemical bonds), like a XPS method. For quantitative analysis EDX is not suitable for light elements, e.g. like oxygen, where it can detect the presence of oxygen, but not the proper quantification. This method works only for thin layer (few microns or less) on the surface and it is quite sensible to contamination current on the specimen.

**Lines 664-681**: Moreover, the measured contact angle for several liquids inside silica and carbon nanopores, indicate the better wettability of the silica walls relatively to the carbon walls and an influence of the pore roughness on the fluid/wall interactions, which is much pronounced for silica than for carbon nanopores. The capillary rise method is the basis of some methods that are widely applied for the determination of contact angles as well as wettabilities of small particles and porous powder materials. For a flat solid surface, many common techniques, e.g. sessile drop and Wilhelmy plate can be applied for measuring contact angles. To determine contact angles of liquids on powders or porous materials, four conditions have to be satisfied for the process (i.e. Washburn’s equation is derived based on these four assumptions): (1) steady state laminar flow, (2) no external pressure, (3) negligible gravitational force and (4) zero velocity of the liquid at the solid/liquid interface (no slip). By comparison, the hydrostatic pressure is much smaller than the capillary pressure, therefore, the liquid rising upward through the tube is primary contributed by the capillary pressure. However, the wettability studies of small particles have always been critical in terms of precision and reproducibility of results. By taking into account the pressure increment and the hydrostatic effects in Washburn equation, it is theoretically possible to derive an improved expression for capillary rise, in order to more accurately describe the relation between the pressure increment and time, which enables to experimentally measure contact angle of small particles precisely.

**Lines 715-733**: The obtained results have indicated an improvement of adhesion effects on the porous silica wall relative to the carbon wall. This method in relation to the studied sample has some limitations. One of them comes from the fact that the samples contain the signal from both: the bulk and the liquid confined in the pores. Therefore, the signal from the confined liquid is often weak and it is difficult to precisely determine the melting temperature. In the future is worth to simultaneously applying another method, e.g. differential scanning calorimetry with slow heating rate or to centrifuge of the sample from the excess liquid. Moreover, in the case of conductive samples, there is a need to use of teflon plate; then above the temperature of 250 K the signal is characterized by an increase, what results from the temperature dependence of electric capacity of teflon material. An advantage of dielectric spectroscopy method is a fact that the method is applied in many fields of research. For solutions far from glass transition, the time scale for molecular motions is in the order of tens of femtoseconds to nanoseconds, so that experiments should be conducted at frequencies in the MHz to THz region. In many aspects, such as the decomposition of the spectra or the interpretation and quantitative analysis of spectral contributions, the technique resembles more conventional spectroscopies. Differences lie in the selectivity—DRS detects the collective fluctuations of species having a permanent dipole moment and a sufficient life time. For example, infrared spectroscopy provides complementary information, although the sensitivity toward collective modes may complicate the interpretation of dielectric spectra.

20. JoVE article does not have a Conclusion section. Please move information in the Conclusion section to Results or Discussion section.

**A conclusion section was moved partially to Results and partially to the Discussion section.**

21. References: Please do not abbreviate journal titles. Please include volume and issue numbers for all references.

**We improved the References. The journal titles were improved, volumes and issue numbers were added for all references.**

**List of changes in the revised manuscript and detailed responses to Reviewers**

**Reviewers' comments:**  
  
**Reviewer #1:**  
Manuscript Summary:  
The author reports the synthesis and characterization of the ordered mesoporous carbon material (OMC) and ordered silica porous matrix SBA-15. They describe the surface properties of mesoporous molecular sieves, their wettability, and the melting behavior of D2O confined in the different ordered porous materials with the similar pore sizes. It is an interesting work which can supply some reference to application of this kind of materials in catalysis or adsorption. The work is well study and written. I think it can be improved if the author can get directly evidence to support the conclusion by using some microtechnique.

**Thank You for this comment. The Conclusion section was moved partially in the body of the Results and Discussion. As the examples of these microtechniques, we can indicate differential scanning calorimetry (DSC), where it would be a supplement of the used by us DS method. XPS microtechnique could be indicate the presence of the functional groups on the surface of molecular sieves.**

**Reviewer #2:**  
This JOVE manuscript describes the synthesis of a mesoporous silica material, similar to the original SBA-15 synthesis along followed by using this material to template the synthesis of ordered mesoporous carbon. The authors characterized the textural properties (nitrogen sorption), wettability, and melting behavior of D2O in the pores.

1. **Reviewer’s comment:**

Why do the authors use the term "mesoporous" throughout the manuscript but use "nanoporous" in the title? This could be confusing for readers. The measured pore sizes for both materials are in the defined mesoporous range so this term should be consistently used.

**Thank You for this suggestion, the “nanoporous” term was used in the whole manuscript. Additional information about the type of materials was introduced in the short abstract:**

**Line 28:** We report the synthesis and characterization of the ordered nanoporous carbon material (called also ordered mesoporous carbon material (OMC)) with the pore size of 4.6 nm and ordered silica porous matrix: SBA-15 with the pore size of 5.3 nm of diameter.

**2. Reviewer’s comment:**

Please use more description on the "dropwise" addition of TEOS, including how long the dropwise addition should take.

**Additional explanations were added in the preparation step (lines 135-137):**

* + 1. After 30 minutes, add the 34 g of tetraethylorthosilicate (TEOS) to the flask. The TEOS addition perform slowly and dropwise while stirring constantly. The drop of whole quantity of TEOS should take 10 min.

**3. Reviewer’s comment:**

Line 193 should be "Nitrogen Sorption" not "Nitrogen Adsorption" to be inclusive of the desorption measurements.

**The more appropriate name of the technique was applied (line 230):**

3.1. Low*-*temperature Nitrogen Adsorption/Desorption measurements.

**4. Reviewer’s comment:**

Why is the tube filled up with "compressed nitrogen" during the prep for the nitrogen sorption analysis?

**The filling the glass tube by compressed nitrogen was performed for** **minimize the weight error. The low-temperature nitrogen adsorption-desorption measurements were performed under nitrogen atmosphere, so** **the weighing the empty glass tube before the measurement should take place under the same conditions. For clarity, the description of this part of the experiment has been rewritten. (lines 232-248):**

* + 1. N2 adsorption/desorption isotherms at 77 K are studied using an ASAP 2020 analyzer (Micromeritics Corp. Norcross, GA, USA).
    2. Use appropriate glass tube for nitrogen sorption measurements. Before to put the porous sample in the glass tube, clean the tube in an ultrasonic washer and rinse with the bi-distilled water and with an anhydrous ethanol.
    3. Heat the glass tube in an oven at 150 °C for 3 hours and fill up the tube with the compressed nitrogen. The weighing the empty glass tube before the measurement should take place under the nitrogen conditions for minimize the weight error.
    4. Fill the tube with the sample, weighing the mass of the sample c.a. 0.20 g.
    5. Prior to the measurements, degas the adsorbents (0.01 mmHg) at 423 K for 24 h. Glass tube with the sample place in degas port of ASAP analyzer. In the degassing port, the sample is connected to the vacuum (5µm Hg) and heated to the set temperature. After degassing, fill the sample with nitrogen and transfer to the analysis port.

**5. Reviewer’s comment:**

3.2.2. These samples are not "dissolving" in ethanol for the TEM grid prep, they are being suspended.

**We agree with this suggestion. It was corrected (line 255).**

**6. Reviewer’s comment:**

The value given for the work of wettability of OMC on line 544 is wrong.

**We have calculated the value again and in our opinion it is correct. The work of immersed wettability in pores We=γl cosθp; if we substitute the obtained value of contact angle in the pores of OMC for D2O equal θp=86.6 ° and if we take the surface tension of D2O equal 71.72 [mN/m], we will obtain the same result, i.e. We=4,2432 [mN/m]. Optionally, it might be approximated to the value We=4.2 [mN/m].**

**7. Reviewer’s comment:**

EDS by nature is not a quantitative measurement, authors need to be careful in making quantitative claims based off of EDS results.

**We agree with this suggestion. Nevertheless**, **TEM/EDS analysis for identify the elements present in the sample can give the indicative quantitative analysis. In this case the differences between carbon and oxygen content were significate and sufficient to establish the conclusions about the hydrophilicity of the carbon surface. Some improvements were incorporated in the text:**

**Lines 635-645:** TEM-EDS spectra images of OMC surface from two different areas of sample are displayed in Figure 4(A) and 4(B). Oxygen and silicon atoms from the OMC surface were detected despite the predominant amount of carbon. The atomic and weight percentage of the elements are presented as insets. The atomic and weight percentage values of all elements obtained from different areas of the samples are similar and indicate about 98% of carbon content and only slightly more than 1 percent of the composition attributable to the oxygen. EDS microanalysis may suggest that the basic character of OMC surface is associated with the very low amount of oxygen-containing functional groups, which are typically predominantly of acidic functionality. Moreover, the basic functional groups can be responsible for the growing of hydrophilicity of the carbon materials. An EDS spectrum of silica matrix confirms the main contribution of oxygen and silicon abundance in the SBA-15 (Fig. 4 (C)).

**8. Reviewer’s comment:**

Line 484, "Transition electron microscopy" is wrong

**We agree with this suggestion. It was corrected. We put “Transmission electron microscopy” in the text.**

**9. Reviewer’s comment:**

On Page 5 the authors describe the results that are presented in Figure 5. The authors claim this result is indicative the "inside of the pores". It is not clear how the authors are certain they are measuring the wettability inside the pores.

**We agree with the comment. The paragraph 3.5.1 was improved following:**

**3.5.1** In order to determine the contact angle inside the pores of studied samples, use the capillary rise method, based on the measurement of the mass rise of the liquid, which is penetrating the porous bed, as the function of the time. **The main assumption of this method is based on the fact that penetrating liquid is advancing into the porous column and that this column is set of intergranular capillaries with a certain average radius. Thus, every relations derived for single capillary are valid for the layer of the porous powder. In a single vertical capillary the wetting liquid floats against the gravitational forces as a result of the difference of pressures between the liquid and the vapor in the pores (capillary pressure). In this meaning, the penetration of the liquid into the porous bed allows to determine the dynamic advancing contact angle inside the pores.**

We applied the modified Washburn equation (Eqn. 2) to determine the value of contact angles inside the pores.

**10. Reviewer’s comment:**

Don't use yellow in the figures in Figure 1, it is too difficult to see.

**The color in the Fig.1 was changed on green.**

**11. Reviewer’s comment:**

This manuscript in its current form is not publishable. It would behoove the authors to seek out a native English speaking individual to assist in final editing and proofreading the manuscript.

**The text was improved and corrected.**